



Preparation of chestnut-like carbon and its application for electrodes with high specific capacitance



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ABSTRACT

Chestnut-like structured carbon comprising platelet carbon nanofibers (PCNFs) grown on selective catalytic gasified activated carbon have shown promising results as application for electrodes. The Ni–Fe catalyst is generally prepared on the activated carbon by immersion process followed by a reduction of temperature at 350–450 °C. The growth of PCNFs then continue on for a predetermined time through the thermal decomposition of ethylene at 600 °C. The resulting structure, which comprises an intimately connected activated carbon and PCNFs, is shown to offer performance advantages with its specific surface properties and electrochemical characterizations. The mesoporous volume is 0.7564 cm³/g higher than that with purely activated carbon (0.1220 cm³/g). The specific surface area is 2401 m²/g higher than those with purely activated carbon (1800 m²/g). The specific capacitance is 136.86 F/cm³ higher than those with P-60.

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1. Introduction

Electrical double layer (EDL) is a structure which determines the variation of potential near a surface, and it has a significant influence on the behavior of colloids and other surfaces in contact with solutions or solid fast ion conductors. Carbon-based materials (activated carbon, carbon aerogel, grapheme and graphene composites) are generally used as electrodes in EDL applications. Among these materials, the activated carbon electrode possesses several desirable properties [1], including ease of processing, high abundance, low cost, inert behavior with respect to corrosion, and increased durability at high operating temperatures [2]. However, despite these advantages, the low degree of crystallization of activated carbon reduces the electrical conductivity of this material. Therefore, the addition of another conductive material, such as carbon black, is necessary to enhance the conductivity of this material [3,4].

The inclusion of a conductive material between the particles and activated carbon establishes an electrical connection based on point contact between the current collector and the active carbon

particles. The conductive material frequently used for this purpose is carbon black. The ratio of the length of fibers to the fiber diameter is large. Hence, the conductive material is used in conjunction with a particulate conductive material, or ash, which is coated onto the fibers and provides excellent electrochemical stability and electrical conductivity [5]. Carbon black particles enhance the electrical conductivity of the other carbon particles, which would otherwise have low conductivity because of the insufficient bulk density of the capacitor. Additionally, it can be challenging to achieve a uniform dispersion of the conductive material, and if the material is poorly dispersed, the electrical conductivity can vary locally within the electrode. Furthermore, the electrical conductivity depends on the quality of the ultra-fine particles of amorphous carbon; the small spherical particles tend to agglomerate into irregular concatenated forms [6].

In the present study, in order to reduce the contact resistance, we investigated the growth of PCNFs on activated carbons, which led to the formation of chestnut-like carbons. Chestnut-like carbons were expected to form close contact with the carbon particles that they were grown on. Therefore, they could interconnect between the particles. As a result, a network consisting of PCNFs and activated carbons was created. Due to the very high electrical conductivity of PCNFs and the intimacy of contact, faster migrations of electrons were anticipated, which in turn, would enhance the electrical properties of the resulting materials. In this paper,

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Table 1

Properties of PCNFs grown on activated carbon without catalytic gasification.

Catalyst (%)	Reaction		Specific surface area (m ² /g)	Total pore volume (cm ³ /g)	Mesopore volume (cm ³ /g)
	Synthesis temp (°C)	Time (min)			
Ni–Fe 1.0	600	30	1222.9	0.7768	0.1623
	750		820.5	0.4307	0.1257
	900		7.3	0.0268	0.0268

we demonstrate the improved electrical conductivity of activated carbons due to the growth of PCNFs on their surfaces.

2. Experimental

Chestnut-like carbon PCNFs were grown on activated carbons with catalytic gasification produced using iron nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Junsei Chemical Co., Ltd., Japan) and nickel nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Junsei Chemical Co., Ltd., Japan) as a catalyst precursor in a thermal chemical vapor deposition reactor. The molar ratios of the metal (4:1 Ni–Fe) to activated carbon (P-60 with a surface area of 1800 m²/g, Kuraray Chemical Co., Ltd., Japan) were 0.1, 0.5 and 1%. Activated carbon (5 g) was added to an aqueous solution (500 ml) that contained the prescribed amount of the metal precursor. Then, the solution was dispersed by 15 min of ultrasonic treatment. The mixtures were then stirred for 24 h at room temperature. The prepared catalysts were filtered and washed with distilled water. Then, the metal catalysts were dried in an oven at 70 °C for 12 h. The activated carbons were then placed in a tubular furnace at 350, 400 and 450 °C for 1 h under N₂/air mixture for catalytic gasification. Following the catalytic gasification, the furnace temperature was raised to 600 °C, at which ethylene was admitted such that the ratio of N₂/C₂H₄/H₂ was 3:1:1 (v/v), which is a total flow rate of 200 cm³/min, during the growth of PCNFs. The PCNFs' growth time was 30 min. Hydrogen (>99.9999%), ethylene (99.9%), and nitrogen (>99.9999%) were obtained from Special Gas Co., Ltd. in Korea and used without further purification. The characterizations of specimens were performed using a scanning electron microscope (SEM) and high resolution transmission electron microscopes (HRTEMs). Surface area analyzer (BELSORP-mini, BEL JAPAN, INC.) was used for the surface area measurements and pore size determination. A electrode cell setup was used to examine the electrochemical performance of various carbons, the activated carbon with catalytic gasification, and the activated carbon with PCNFs. A carbon electrode was made by pasting the slurry of the carbon, 0.01 g of the poly(vinylidene) fluoride binder, and 8 ml of dimethylacetamide (DMAC) onto a glassy carbon substrate. The dried electrode was then transferred to the electrochemical cell and CV measurements were recorded in argon-saturated 1 M NaCl. The CV measurements were carried out with an AutoLab PGST30 potentiostat. The electrolyte was prepared from a 1 M NaCl solution using the Ag/AgCl reference electrode. Pt wire was used as the counter electrode. The scan range was fixed at –0.4 to 0.6 V with sweep rates of 20.0, 50.0, and 100.0 mV/s to measure the mesopores and micropores. The electrolyte temperature was maintained at room temperature.

Table 2

Properties of chestnut-like carbon for each of the synthetic conditions.

Catalyst (%)	Reaction			Specific surface area (m ² /g)	Total pore volume (cm ³ /g)	Mesopore volume (cm ³ /g)
	Gasification temp (°C)	Synthesis temp (°C)	Time (min)			
Pristine AC				1708.2	0.7768	0.1220
Ni–Fe 1.0%	Non-gasification	600	30	1222.9	0.7768	0.1623
	350			1776.5	0.9113	0.7276
	400			1728.6	1.2100	0.7564
	450			1171.0	0.9956	0.7396

3. Results

Many studies have focused on the mechanism of activated carbon with catalytic gasification, but only a few papers have dealt with the formation or control of the porous structure in carbon materials formed by catalytic gasification [7]. Table 1 summarizes the surface characterization of grown PCNFs on activated carbon without catalytic gasification. The maximum specific surface area of PCNFs grown on activated carbon with 1.0% Ni–Fe catalyst was between 7.3 and 1222.9 m²/g with a peak value of 600 °C. Its mesopore volumes were 0.1623, 0.1257, and 0.0268 cm³/g for 600, 750 and 900 °C, respectively. According to the survey, the catalytic gasification appears to affect the catalytic activity of the Ni–Fe catalyst on the activated carbon. According to the synthetic temperature, the specific surface area and mesopore volume of the grown PCNFs on activated carbon without catalytic gasification decreased, irrespective of the amount of PCNFs produced. The micropores that contributed to the large surface area must still be close to the PCNFs' growth on the catalyst particles.

Table 2 summarizes the surface characterization of chestnut-like carbon. The catalytic gasification of activated carbon in air restored the surface area and the pore volume over those of the pristine activated carbon. The chestnut-like carbon had a higher surface area compared to the PCNFs grown on activated carbon without catalytic gasification, while 1.0% Ni–Fe catalytic gasification samples showed a surface area of 1171–1776 m²/g. The maximum mesopore volume of chestnut-like carbons with the 1.0% Ni–Fe catalyst was between 0.1623 and 0.7564 m³/g with a peak value of 400 °C at gasification temperature. After impregnation of the pristine activated carbon with 1% Ni–Fe catalyst at 450 °C, the surface area decreased significantly to 1171 m²/g. A trend toward reduction in the specific surface area and enlargement in mesopore volume were observed with an increase in catalytic gasification temperature.

All of these measured mesopore volumes are higher than the 0.1623 cm³/g for the pristine carbon, as shown in Fig. 1(A). The chestnut-like carbon increased the maximum mesopore volume up to 466%, as shown in Fig. 1(B). Fig. 1(A) and (B) shows the maximum specific surface areas as being 2401.5, 1832.8, and 1776.5 m²/g for the chestnut-like carbon formed with catalyst contents of 0.1, 0.5, and 1.0%, respectively. Accordingly, the pores of the activated carbon were blocked by an excessive deposited catalyst. When the pristine activated carbon was impregnated with a 0.1% Ni–Fe catalyst at 450 °C, the surface area increased significantly to 2401.5 m²/g. The content of the catalyst was considered an important factor in this research. The selection of the appropriate amount

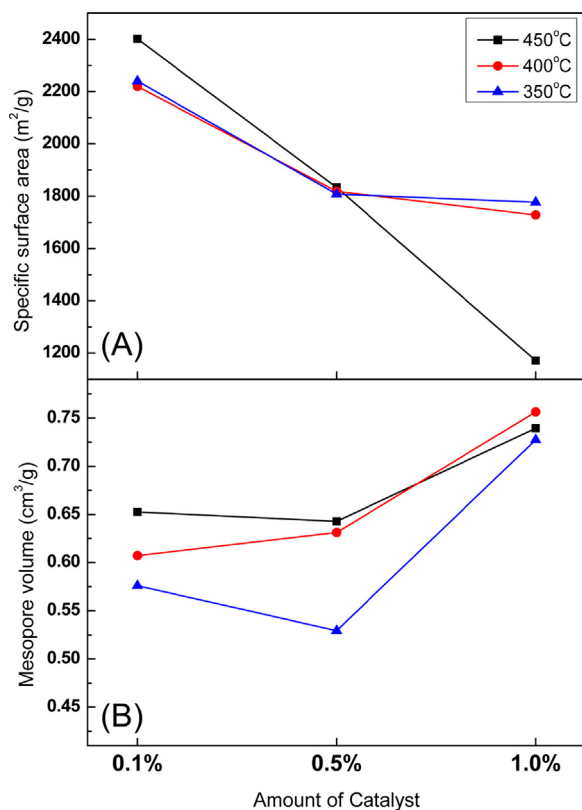


Fig. 1. Surface properties of PCNFs grown on activated carbon with 0.1, 0.5, 1.0% Ni–Fe catalytic gasification at 350, 400, and 450 °C (A) specific surface area and (B) mesopore volume.

of catalyst for the catalytic gasification process was found to significantly affect the desired increase in porosity.

The PCNFs synthesized on the non-gasified activated carbon grew significantly more than the PCNFs synthesized on activated carbon with catalytic gasification. The surface area of the activated carbon became highly porous after catalytic gasification, as shown in Table 2. The epitaxial growth of PCNFs on the activated carbon surface could be suspected, even though the PCNFs grown on the catalyst particles were dispersed on the activated carbon surface. The entangled PCNFs are likely to fill more open space in the pores of the activated carbon. Overall, according to Fig. 2, the PCNFs grown on the activated carbon were not straight, but instead exhibited entanglements and nodes along their axes. The PCNFs sitting on the activated carbon indicated the generation of an intimate contact region between the PCNFs and the activated carbons. Such intimate contacts, and the interconnections of PCNFs among the activated carbon, have been forecasted to improve the electrical conduction between the activated carbon supports. This looks like a similar shape of the chestnut.

Fig. 3 shows a TEM image of chestnut-like carbon with a 1.0% Ni–Fe catalyst. The individual sheets of the graphite-like lattice can be observed and are predominantly ordered in a platelet structure. Consequently, the edges of the graphene layers are exposed [8]. TEM studies revealed that the samples generated from the interaction of C_2H_4/H_2 with Ni/Fe were highly graphitic with structures in which the graphene sheets were aligned perpendicular to the fiber axis. PCNFs have a surface area that is almost an order of magnitude lower than that of activated carbon. Hence, their performance in this separation process is far superior. Thus, the free edges of the PCNFs are expected to perform surface functions cooperatively [9].

CV measurements have been widely used to characterize the electrosorption properties of electrodes. Fig. 4 shows the CV curves of the activated carbon and catalytically gasified activated carbon electrodes at a scan rate of 50 mV/s in a 1.0 M NaCl aqueous solution with a potential window of –0.4 to 0.6 V. The influence of the catalyst composition on the electrosorption performance of the catalytically gasified activated carbon electrodes was systematically investigated [10].

Fig. 5 shows that the specific capacitances of chestnut-like carbon are significantly higher than those of other activated carbons. With increasing mesopore contents, the specific capacitance of the electrodes first increased to its highest value and then dropped significantly. This result is explained as follows. The chestnut-like carbon surfaces provide an overall conductive architecture in the composites, which results in the improved electrosorption properties of the activated carbon. The chestnut-like carbon can improve the accessible surface area of the activated carbon. The PCNFs can directly provide additional channels, and thus, a larger surface area that is accessible to ions that enter the inner pores. The PCNF surface possesses an overall higher porosity, which leads to an enhanced mass transport. The highest specific capacitance was found for chestnut-like carbon fabricated with the Ni–Fe 0.1% catalyst at 450 °C.

4. Discussion

The crystallinity of the PCNFs grown on activated carbon were examined and compared to that of the activated carbons. Fig. 6 shows an XRD spectrum of activated carbons before and after the growth of PCNFs. For the activated carbons, weak and broad (002) and (100) peaks are seen. The crystallinity appears to have improved due to the existence of the PCNFs, as shown by the upper spectral line. The d-spacing of the crystalline activated carbon was found to be 0.205 nm, which corresponds to the (100) planes. It seems that the seeding of the catalyst particles on the carbon surface occurs at or near the crystalline regions.

Oya et al. found that the number of pores increased as the amount of catalyst and reaction temperature increased [11]. The increase in the specific surface area because of catalytic gasification showed similar trends, as shown in Table 2. In particular, the mesopores of catalytic gasification at 450 °C contained the largest surface area, with a specific surface area of 0.6060 cm³/g. However, the mesopore count was reduced for the 1.0% Ni–Fe catalyst. The catalyst surplus prevents pores from forming in the activated carbon. Therefore, the use of the optimal amount of a gasified catalyst is important to create more mesopores.

The diameter of the PCNF is known to depend on the catalyst's size [12]. The catalyst particles dispersed on the carbon surface can be sintered with other nearby particles, thereby forming larger particles through catalytic reduction in hydrogen at high temperatures, such as 600 °C [7]. Fig. 7(a) demonstrates that catalytic gasification in the air after catalyst deposition on the activated carbon resulted in a sharper increase in surface area, which was accompanied by the additional development of mesopores relative to the number of pores in the starting activated carbon. This graph indicates that the PCNF raw materials had peak pore sizes of 3–5 nm, which gradually increased to approximately 10 nm. In the pore width range of 4–5 nm, the >450 °C catalytic gasification samples maintained sharp peaks, while the 350 °C catalytic gasification samples showed no peaks or peaks that were shifted to smaller value areas in the distribution.

Additionally, Fig. 7(b) summarizes the calculated mesopore volumes of PCNFs grown at the reaction temperature of 450 °C. Mesopore volumes of 1.425, 1.1953, and 0.9956 cm³/g are produced when 0.1, 0.5, and 1.0% Ni–Fe catalytically gasified activated

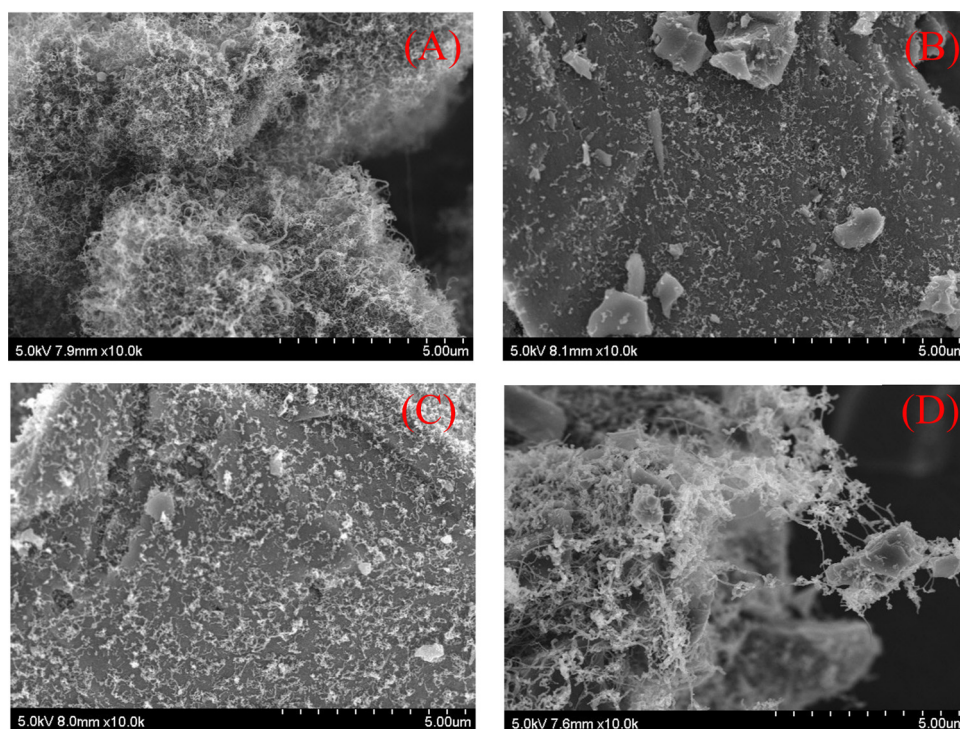


Fig. 2. SEM images of (A) PCNFs grown on activated carbon without catalytic gasification, (B) PCNFs grown on activated carbon with catalytic gasification at 350 °C, (C) at 400 °C, (D) and at 450 °C.

carbon is provided. Therefore, chestnut-like carbon (1% Ni–Fe catalytic gasification at 400 °C) showed mesopore volumes that were 0.7564 cm³/g higher than the mesopore volume of the pristine activated carbon (0.1220 cm³/g). Chestnut-like carbon (1% Ni–Fe catalytic gasification at 400 °C) formed a pore system with a different three-dimensional structure in which the pore structure and morphology were disrupted by the formation of voids near the carbon surface and PCNF.

Fig. 8 illustrates a schematic model of the overall process approach, identifying the steps from catalyst deposition on the activated carbon to catalytic gasification of the activated carbon containing the catalyst and chestnut-like carbon surface. In this model, the activated carbon micropores described by Lim and Yoon are simply depicted as rectangular shapes [7], which can be considered the side view of a cylinder, although the real morphology and structure of the micropores may be more complicated. Mesopores

measuring 3–4 nm in size were connected to each other; the space between the pores was either covered by fish skin-like species or was observed as a closed-layer structure produced by deformed basal graphite planes on the surfaces of the individual fibers. The surface roughness, defined as the ratio of the measured topographical surface to the chosen geometric surface [13], was suggested to have resulted from these mesopores [14]. This product was successfully prepared by catalytic gasification and PCNFs grown on activated carbon after the catalyst impregnation step. However, the surface areas of the products were limited to <1200 m²/g when the PCNFs grew on activated carbon without any catalytic gasification steps. Hence, the catalytic gasification step was found to be important for obtaining both surfaces of the activated carbon. Additionally, the high surface area values (2200–2400 m²/g) achieved by catalytic gasification prior to PCNFs grown on activated carbon suggest that a significant amount of micropores exist on the activated

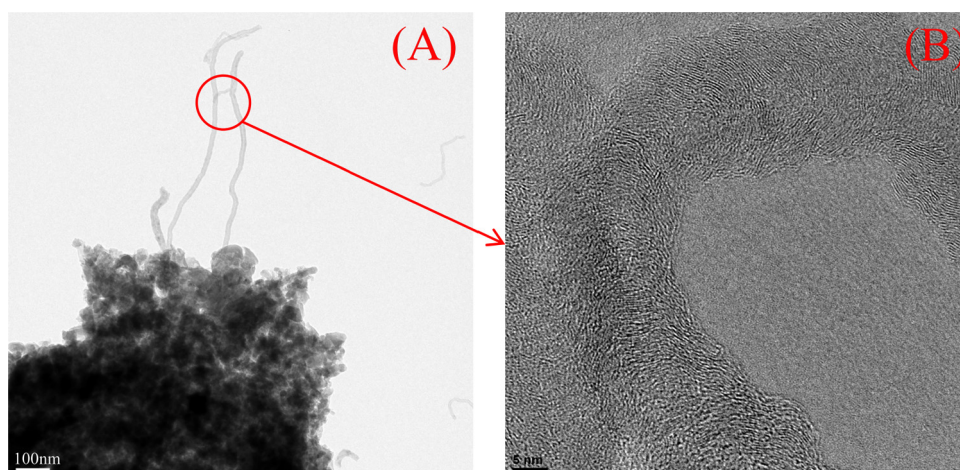


Fig. 3. TEM images of (A) chestnut-like carbon and (B) PCNF grown on catalytic gasified activated carbon with 1.0% Ni–Fe catalyst.

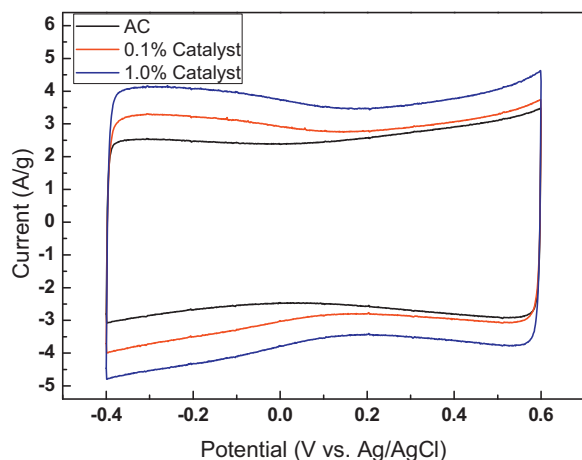


Fig. 4. CV curves of activated carbon and catalytic gasified activated carbon with several different catalyst contents measured at 50 mV/s in a 1.0 M NaCl aqueous solution.

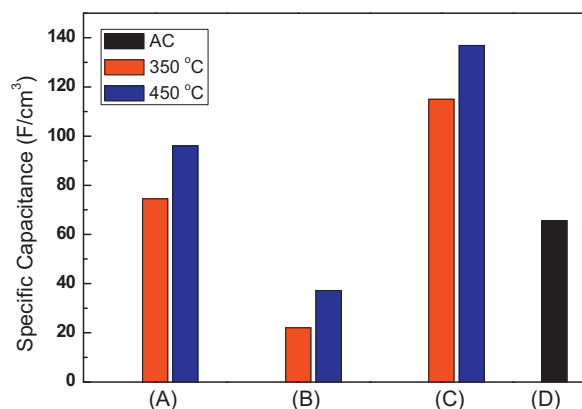


Fig. 5. The specific capacitance of (A) catalytic gasified activated carbon with 1% Ni-Fe catalyst content, (B) PCNF grown on non-gasified activated carbon at 600 °C, (C) PCNF grown on activated carbon at 600 °C after using catalytic gasified activated carbon with Ni-Fe 0.1% catalyst at 350, 450 °C, (D) and pristine activated carbon.

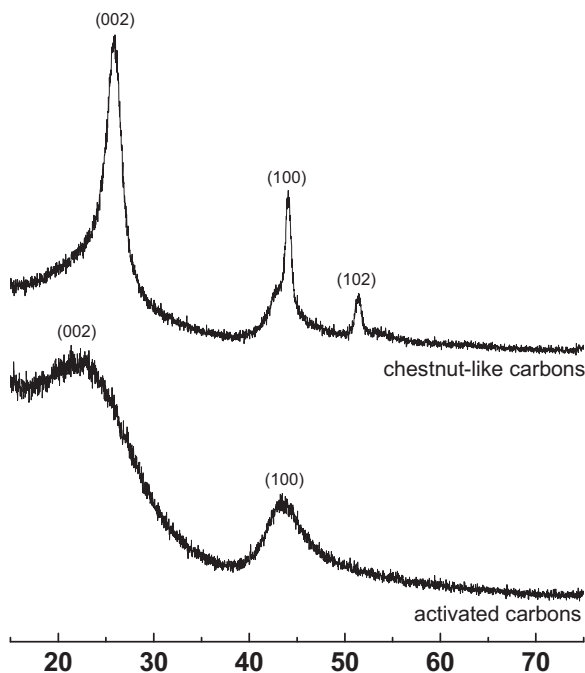


Fig. 6. X-ray diffraction patterns of activated carbon after the growth of PCNFs at 600 °C for 30 min.

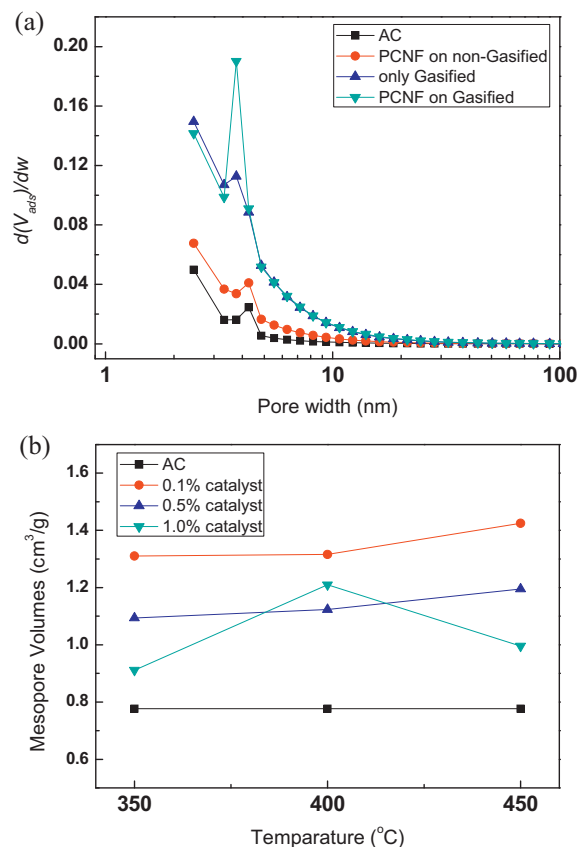


Fig. 7. Pore size distributions calculated by the BJH procedure of activated carbon (a) with various PCNFs growth conditions, and (b) with various Ni-Fe catalyst content.

carbon and continue to contribute to the surface properties of the composites. Thus, the free edges of the PCNFs and the micropores of the activated carbon are expected to perform surface functions cooperatively.

Additionally, the consumption of the carbon in proximity to the catalyst particles during the process of catalytic gasification appeared to partially open pores blocked by the catalyst particles, as illustrated in Fig. 8(a). However, the surface area of chestnut-like carbon was reduced when the catalyst added was 1.0% Ni-Fe. The surplus of catalyst particles prevented the formation of pores in the activated carbon. Therefore, the selection of a proper amount of catalyst is important for the creation of additional surface area.

The specific capacitance of the activated carbons is affected by the surface area and pore size distribution. Additionally, the capacitance is mainly influenced by the pore size of the materials [15]. A wide range of literature is available on the influence of surface area on the specific capacitance of electrodes. Generally, the specific capacitance is directly proportional to the specific surface area. Hence, the specific capacitance of a material is expected to increase with the effective thickness of the EDL. However, this is not necessarily valid for all carbon materials [16]. More commonly, the electrosorption capacitance of the electrode is higher at lower scan rates. This phenomenon occurs because ions diffusing from the solution have more access to the electrode surface, which leads to an enhanced surface adsorption/desorption of ions. The chestnut-like carbon electrodes show approximately 71.17 F/cm³ retention of the specific capacitance, which is higher than that of the activated carbon.

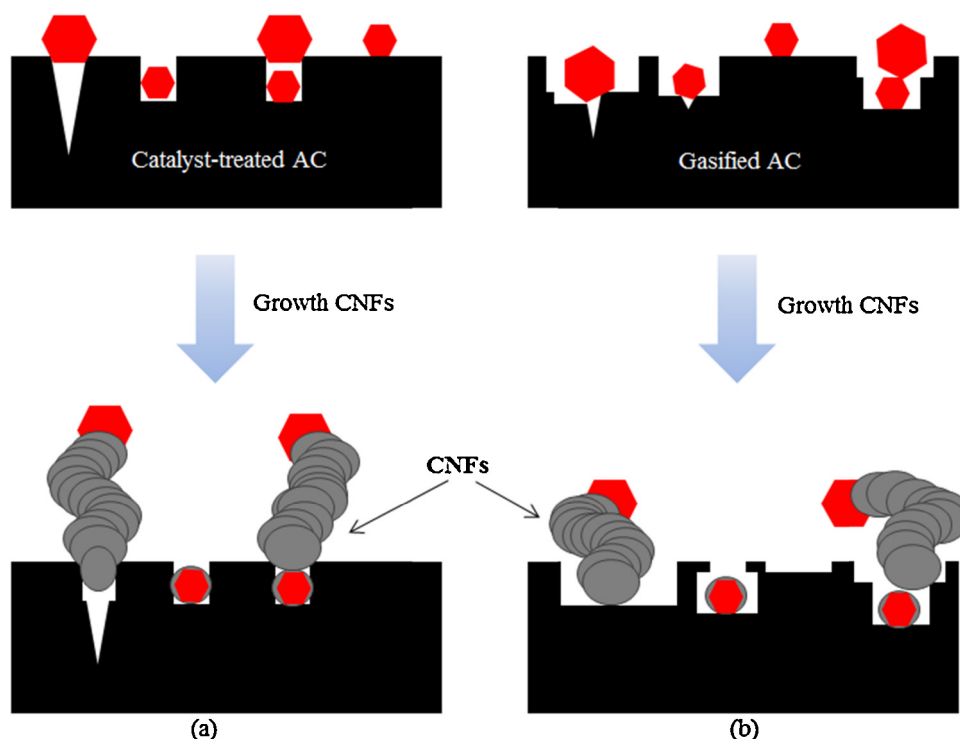


Fig. 8. An illustration of multi surface activated carbon formation by catalyst impregnation and PCNF synthesis (a) without catalytic gasification (b) with catalytic gasification [6].

5. Conclusions

In this work, new carbon materials were made using the catalytic gasification of activated carbon and PCNFs grown on the activated carbon. The work is summarized as follows. First, the chestnut-like carbon was prepared through catalytic gasification with Ni–Fe catalysts in air. Catalytic gasification was shown to be a very effective means of producing a useful porous carbon material as long as the catalyst and the gasification conditions are carefully selected. Second, the pore size was controlled through growing PCNFs on activated carbon using catalytic gasification. The surface area of chestnut-like carbon was $2401 \text{ m}^2/\text{g}$ when 0.1% Ni–Fe catalytic gasification was used at 450°C . This value was $600 \text{ m}^2/\text{g}$ higher than the specific surface area of the pristine activated carbon. Finally, chestnut-like carbon was found to show better performance due to a high specific surface area. Additionally, this study improves the adsorption/desorption performance rating and electrical performance evaluations of MEA in fuel cells and advances the CDI process.

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